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We have utilized an iodine absorption cell to enable detailed Raman studies at low frequency (down to 15 cm^{-1}) in a thin film of the high-temperature superconductor $Ba_2YCu_3O_7$. Subtraction of spectra just above and well into the superconducting phase reveals a weak broad feature (maximum near 400 cm^{-1}, half width at half maximum approximately 250 cm^{-1}), which we tentatively interpret as due to scattering near the superconducting gap. The large width of the feature may be partially related to smearing of the transition, or to gap anisotropy. Its onset near 200 cm^{-1} suggests an energy gap 2Δ near 25 meV. Assuming that the surface region probed in the scattering has the same T_c as that measured for the overall film (onset 85 K), we obtain the ratio $r = 2\Delta/k_BT_c = 3.4 \pm 1.5$, consistent with the BCS weak-coupling value of 3.5.

Considerable interest of both a scientific and a technological nature has been generated by the recent discovery of a class of compounds which exhibit superconductivity at temperatures near 100 K. After the initial report,[1] the correct composition ($Ba_2YCu_3O_7$) was quickly found,[2,3] and a large number of related compounds with similar behavior were discovered within weeks.[4,5] Theoretical questions surround the applicability of BCS theory to these materials. Accordingly, studies have been undertaken to determine the value of the superconducting gap Δ, since one clearcut prediction of BCS theory is that the ratio $r \equiv 2\Delta/k_BT_c$ should be 3.5 in the weak-coupling limit. Here k_B is the Boltzmann constant and T_c is the superconducting transition temperature. Tunneling measurements[6,7] have indicated values as high[7] as $r = 13$, but the most complete infrared study to date[8] has suggested $r = 3.5$ as the most probable value. Other tunneling measurements[6,9,10] give values ranging from 4.5 to 10.5. Lee and Read[11] have pointed out the potential importance of inelastic scattering processes in causing high r values. On the other hand, Anderson[12] has recently suggested that the new high-T_c materials are in fact zero-gap superconductors. Given the uncertainties apparent from both a theoretical and an experimental viewpoint, it appeared advantageous to use Raman scattering as yet a third probe of the same quantity.

Raman scattering has been used to study superconducting gap transitions previously.[13,14] Klein[13] has reviewed the theory for an isotropic gap superconductor, and Guden[15] has considered in more detail the subtle influences of matrix element effects. The features observed[13,14] are usually rather weak and broad compared to typical allowed phonon scattering.

Several Raman studies of the high-T_c superconductors have already appeared, and we shall not attempt to review them all here. A number of Raman-active modes have been identified[16] and a subsequent study[17] of the spectra as as function of oxygen stoichiometry has proved amenable to analysis within a simple force-constant model. None of the studies reported to date, however, has been successful in detecting evidence of gap scattering. The primary reason for this is instrumental, since a glance at the spectra reported makes it obvious that a weak broad feature below about 400 cm^{-1} would be impossible to discern from the instrumental wing caused by the elastic scattering at the surface, even in the relatively clean spectra reported by Macfarlane, Rosen, and Seki.[16] Accordingly, we have attempted in the present study to utilize the iodine absorption cell technique[18] to uncover any scattering in the region of primary interest, near where the gap is expected (200–300 cm^{-1} under BCS weak-coupling theory).

The results of this study show that there is indeed a broad feature which develops in the superconducting phase, with a very broad maximum in the vicinity of 400 cm^{-1}. Although we tentatively identify this feature as due to scattering at the gap, the breadth of the feature precludes any accurate determination of Δ, in a manner similar to the situation in the ir spectra of Thomas *et al.*[8] The interpretation we place on this feature below, in support of the value obtained in the ir work, must be viewed as tentative and awaiting confirmation in other samples and by other means.

The sample used for this study was a thin film produced by dc magnetron sputtering from a composite oxide target.[19] The film was deposited onto a $SrTiO_3(100)$ substrate with a composition of $Y_{1.1}Ba_2Cu_3O_x$ as determined by Rutherford backscattering spectrometry. Subsequent heat treatment at 900 °C in an oxygen atmosphere was used to produce a superconducting film with a relatively sharp transition in the range 70–85 K.[20] The resistivity was measured with indium electrodes, which were attached to small areas on the sample surface, and the material was found to exhibit zero resistivity below 70 K (Fig. 1, inset). X-ray diffraction revealed that the majority phase in the film is the orthorhombic $Ba_2Y_1Cu_3O_x$ phase.[3] The sample is polycrystalline, with no preferred crystallographic orientation. A film sample was employed in an effort to improve the surface quality for the scattering experiment. This effort largely failed in its intent, since the crystallites formed during heat treatment caused scattering similar to that from a polished ceramic surface. However, the film sample was still deemed preferable since no polishing or other handling was needed in its

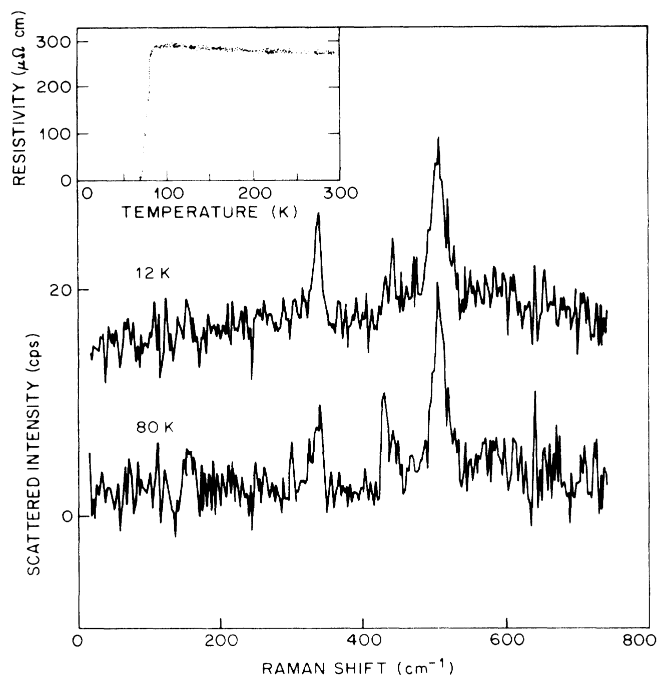

FIG. 1. Two spectra of $Ba_2YCu_3O_7$ obtained at low power density at the nominal temperatures indicated. The iodine fluorescence has been subtracted, using the iodine line at 637 cm^{-1} as an intensity guide. The iodine absorption structure is negligible here relative to the noise, and the spectrum has *not* been normalized to remove that structure. The 12 K trace is offset upward by 15 cps for clarity. The inset shows the resistivity measured on the same sample as a function of temperature, with the arrows indicating the nominal temperatures of the spectra.

preparation. The sample was mounted mechanically on a Cu stage inside a flowing He gas cryostat, operating under 1 atm of He exchange gas for cooling.

The phonon spectrum we observed was similar to that reported by others. Although we never observed visual laser damage to our sample, preliminary work with the sample in pumped helium below the λ point showed that, even with a line focus of dimension 2×0.2 mm^2, it was necessary to work at a power density of about 5 W/cm^2, far below that employed in previous work,[16] in order to avoid bubbling. Since cooling in exchange gas is far less efficient than in liquid, we maintained this power density even at higher temperatures, in order to reduce heating to a minimum. Thus, it seems reasonable to estimate our heating at 5–10 K. (This is substantially larger than the estimate given by Macfarlane *et al.*[16] since our power density is 10 times lower than theirs.) In addition to the apparent need to work at low power, the physical arrangement of the Dewar restricted our collection angle to $f/3$ as well. These two factors conspired to reduce our signal by a total factor of about 20 from that obtained by Macfarlane, for example, who used a power density of 50 W/cm^2. It was, however, possible to obtain usable spectra in a few hours of averaging time. The incident wavelength was 5145 Å from an Ar^+ laser operated single mode and tuned to the iodine absorption. The scattered light traversed an iodine absorption cell before being focused onto the entrance slit of a double monochromator equipped with holographic gratings (1800 l/mm). The spectral slit width was 7 cm^{-1}. The throughput of the iodine cell was about 50%. The incident and scattered polarizations lay in the scattering plane. The incidence angle was 65° from the normal. The collection axis was at right angles to the incident beam.

Correction of the spectra for the iodine absorption was unnecessary due to the very large slit width employed and to the low signals. However, the light reemitted as fluorescence from the iodine cell, even though not focused on the slit, constituted a substantial interference in the spectrum. There were three main narrow lines which resulted from this fluorescence at 215, 426, and 637 cm^{-1}. These are removed from the data displayed by subtraction of a spectrum taken with the image of the scattering volume moved 1 mm off the entrance slit. The scaling of this subtraction was adjusted to remove the strongest of the lines (637 cm^{-1}), which was isolated in the $Ba_2YCu_3O_7$ spectrum with an intensity about twice that of the strongest phonon mode. The only substantial difficulty introduced by this procedure lay in the near coincidence of the fluorescence line at 426 cm^{-1} and the phonon line near 438 cm^{-1}, the latter being significantly weaker. This difficulty, however, had no appreciable influence on the broad feature attributed below to the gap scattering.

Spectra obtained at nominal temperatures of 80 and 12 K are shown in Fig. 1. (Temperatures are not corrected for the laser heating estimated to be 5–10 K.) Although the spectra are noisy due to the factors noted above, we note that the major features evident there (at 338, 440, and 506 cm^{-1}) lie in good agreement with previous reports.[16,17] The fact that we find no evidence of the features at 470 and 625 cm^{-1} (which was also true at higher power and temperature) indicates that our samples are predominantly orthorhombic, since these lines have been identified[17] as attributes of the tetragonal phase.

The difference in the apparent intensity and position of the 440 cm^{-1} peak is apparently due to imperfect subtraction of the I_2 fluorescence mentioned above. Disregarding this artifactual difference though, there remains a small difference between these spectra discernible in Fig. 1, which may be made more obvious by subtraction and averaging of the data. In Fig. 2 we show the result of subtracting the spectrum at 80 K from the one at 12 K, with subsequent averaging over a range of 15 cm^{-1}. As may be seen in the figure, the result is a broad spectral feature, with maximum intensity near 400 cm^{-1} and with an intensity about an order of magnitude smaller than that of the strongest phonon peak at 506 cm^{-1}.

Given that this scattering feature is apparently due to having entered the superconducting phase on cooling from 80 to 12 K (nominal temperatures, uncorrected for laser heating), we attribute it to scattering from the electronic states near the gap. However, we believe that it is incorrect to identify the peak with the value of 2Δ, since the gap scattering should appear as a highly asymmetric feature in the spectrum, with its limit on the *low* side cor-

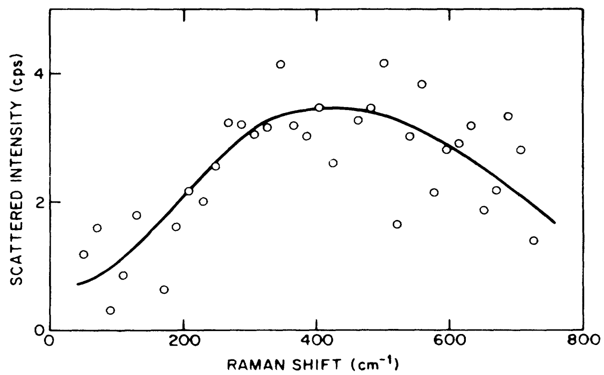

FIG. 2. Result of subtracting the 80 K spectrum in Fig. 1 from the one taken at 12 K. Each point is an average over a range of 15 cm^{-1}. The line is a guide to the eye.

responding to the gap. In fact, the theory of Klein[13] yields a cusp at $\omega = 2\Delta$, with zero intensity for $\omega < 2\Delta$. In an anisotropic material we expect this feature to be smeared out, but to retain its fundamental asymmetry. Indeed, the more detailed theory of Guden[15] shows this effect quite clearly. Although the latter calculation shows good qualitative agreement with our observed peak shape, the data shown certainly do not permit any detailed comparison with the theory. We may, however, use the data to estimate the value of the gap.

From our data, it appears that the gap lies near or even below $2\Delta = 200$ cm^{-1} (25 meV). Using the bulk superconducting onset temperature of $T_c = 85$ K, we obtain $r = 3.4$. This interpretation is consistent with that of Thomas *et al.*[8] The extreme breadth of the feature, which precludes a more accurate determination of r, may result from smearing of the transition from a defected surface layer (see below) or from gap anisotropy. We emphasize, however, that our data are definitely not compatible with values of r in the range of 10–13 if $T_c = 85$ K, since the corresponding frequency would be 600–800 cm^{-1}.

We note also that Thomas *et al.*[8] have speculated that some region near the surface may not become superconducting even at very low temperature. It is important to point out in this regard that the penetration depth for our light is not known, but is certainly closer to 1000 Å than to the 10-μm penetration estimated in the ir region.[8] Thus, a surface layer with depressed T_c would have a larger influence on our spectra than on the ir region, and might also account for the very weak intensity we observe. In the above calculation of r we have used the bulk value of T_c. If T_c is substantially reduced in the surface layer active in our scattering process, then the correct value of r would be increased accordingly. We note also that such a surface layer might contribute to a smearing of the apparent gap peak.

Note added. After final preparation of this manuscript, we became aware of an independent study by Timofeev and co-workers,[21] where similar results were obtained, albeit with a somewhat higher value of Δ.

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